CHRISTINA MCGRAW

High-resolution Measurement of Seawater Carbonate

Since the start of the Industrial Revolution, the chemistry of seawater has been significantly changed by the absorption of fossil fuel CO_2 (carbon dioxide) from the atmosphere. When CO_2 is absorbed by seawater, it sets off a series of chemical reactions: carbonic acid (H_2CO_3) is formed, which then dissociates to H_3O^+ and bicarbonate (HCO_3^-). The H_3O^+ reacts with carbonate ions (CO_3^{2-}), forming additional bicarbonate. The overall reaction is the production H_3O^+ and the consumption of carbonate, a process referred to as ocean acidification.[1]

Ocean acidification has already led to a 30 percent increase in the concentration of seawater H_3O^+ (increasing the acidity and reducing the pH) and a 10 percent reduction in the concentration of carbonate. Under the IPCC's 'business as usual' scenario (RCP 8.5), increasing CO_2 emissions will lead to a further 100 percent increase in ocean H_3O^+ and a further 60 percent decrease in carbonate concentration by the year 2100.

These changes may have a profound effect on calcium carbonate structures: when the pH and carbonate concentrations become sufficiently low, these structures are no longer stable. There is increasing evidence that the construction and maintenance of calcium carbonate shells and skeletons by many calcifying organisms (e.g., calcifying algae and molluscs) will become increasingly difficult.[2] However, the extent to which individual species will adapt to the changing ocean is difficult to predict. A species' ability to thrive in the changing oceans will depend on a range of factors, including (a) its ability to maintain carbonate structures as carbonate becomes increasingly scarce; (b) the extent to which the local seawater has equilibrated with atmospheric CO_2; and (c) short-term processes that influence or perturb that equilibrium. Understanding local variability (b and c) is confounded by seasonal, daily and tidal fluctuations, which can be greater than the ocean acidification-driven changes predicted by the end of the century.

However, while pH and local variability is relatively straightforward to measure in the field, carbonate concentration is difficult to measure directly. Instead, carbonate is calculated from bulk seawater samples brought back to the laboratory and analysed for at least two of the carbon chemistry parameters (pH, partial pressure of CO_2, dissolved inorganic carbon, and alkalinity).[3] This time-consuming process limits the temporal and spatial resolution of carbonate measurements.

In order to address this limitation, our laboratory has developed a range of hand-held sensors to measure fine-scale carbonate changes in the field. The sensors highlighted in this artwork use optical fibres to direct light to the surface of calcium carbonate structures[4]. By 'seeing' how the surface changes, we can study its fundamental behaviour: *When do we see a breakdown of calcium carbonate? Why do we see breakdown when theory tells us the system is stable? How do our expectations change as we delve 1km below the surface? 5km? 10km?* By exploring the subtle changes to carbonate structures, we are increasing our understanding of both ocean acidification and the chemical relationships that form the basis of our future ocean predictions.

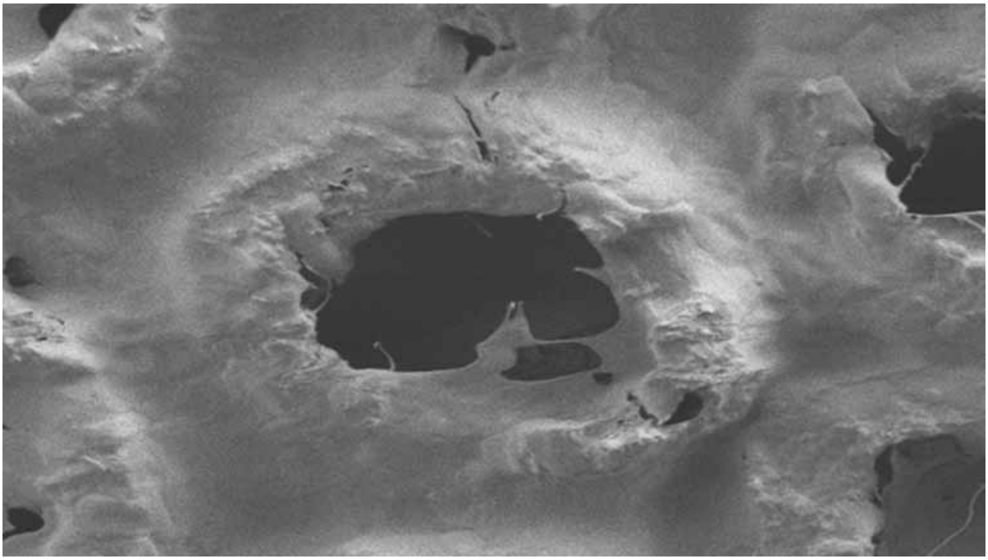

Figure 1. Scanning electron microscope image of local calcifying algae exposed to low-pH seawater.

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1. Cliff S Law et al., "Ocean Acidification in New Zealand Waters: Trends and Impacts," *New Zealand Journal of Marine and Freshwater Research*, 52:2 (2018), 155-95, doi: 10.1080/00288330.2017.1374983.
2. Anaëlle J Lemasson, Stephen Fletcher, Jason M Hall-Spencer and Antony M Knights, "Linking the Biological Impacts of Ocean Acidification on Oysters to Changes in Ecosystem Services: A Review," *Journal of Experimental Marine Biology and Ecology*, 492 (2017), 49-62, doi: 10.1016/j.jembe.2017.01.019.
3. *Guide to Best Practices for Ocean CO_2 Measurements*, PICES Special Publication 3, eds AG Dickson, CL Sabine and JR Christian (Sidney, BC: North Pacific Marine Science Organization, 2007), http://cdiac.ess-dive.lbl.gov/ftp/oceans/Handbook_2007/Guide_all_in_one.pdf.
4. Christina M. McGraw, Christopher Cornwall et al, "An automated pH-controlled culture system for laboratory-based ocean acidification experiments," *Limnol. Oceanogr.: Methods* 8, 2010, 686–694, available at https://www.otago.ac.nz/oceanacidification/otago052693.pdf

HOPE DUNCAN

What if the Jellyfish Became Encrusted with Calcium Carbonate?

Our oceans make up 70 percent of the earth's surface.[1] They are some of the most unexplored and abundant corners of the world, and we are contributing to their demise.

Our actions through carbon dioxide emissions, waste production and waste disposal – to name a few of our impacts – are significant contributors to climate change, a world-wide problem caused by increases in temperature resulting in the warming of our oceans. At the same time, the oceans are absorbing increasing amounts of carbon dioxide, which decreases pH levels (and so increases acidity). This decrease in pH is causing issues for many marine inhabitants, especially those with calcium carbonate shells and structures.[2] This work is a response to this problem, known as ocean acidification.

The pre-average pH in 1850 was 8.2, the current average is 8.1.[3] This rise in acidity levels is blocking the growth of marine organisms that rely on calcium carbonate for either skeletal or protective structures, and causing corrosion of existing structures instead of enabling growth.[4] Among the marine organisms affected by these changes are corals and fish. New corals cannot grow, and existing corals are being corroded, resulting in the decimation of reefs and a lack of nurseries for juvenile fish. In addition, ocean acidification is also impacting on the ability of fish to mate and produce offspring.[5] The demise of fish, corals and shellfish favour the spread of jellyfish as there will be less competition for food and predicted algae blooms, both favouring acidification-resistant jellyfish.

The jellyfish is one of our most beautiful ocean inhabitants, but also one of the most dangerous. Their fluid-like movement through water is captivating. But with increasing levels of ocean acidification, jellyfish are one of the species that will flourish.[6] While marine organisms with shells and structures formed from calcium carbonate will begin to dissolve with increased acidification, jellyfish are surprisingly resistant to these changes and will become abundant due to less competition for food.[7]

But what if the jellyfish became encrusted with calcium carbonate? They might still possess their beauty, but that mesmerising movement would be lost. We know that ocean acidification will not cause encrustation of jellyfish. However, this work aims to provoke ideas and images of the extreme in order to get the viewer to engage in the reality of the situation.

Within the jellyfish work, the fibre optics and crystals hint at the work being done by Dr Christina McGraw and her team to understand how ocean acidification is affecting our marine environment. The jellyfish is made from a material that offers a possible solution to part of our waste production problem: wool – a biodegradable, natural, organic alternative to many plastics and polymer materials. The rigidity of the crystallised pieces shows loss of function.

It is hoped that the beauty of this piece will remind viewers of what an incredible marine world we have, and get them thinking about what they can do to help preserve it.

The jellyfish is displayed in a blacked-out dressing room, to eliminate light disruption. We anticipated that to engage with the work, people would step into the exhibition space with the jellyfish and enclose themselves for a full immersive experience. However, watching how people engaged during the exhibition, three groups emerged: those who peeked behind the curtain but kept moving, as they failed to understand the expectation; those who popped their heads in but did not close the curtain, resulting in a lot of diffused light; and those who stepped right in and closed the curtain around themselves.

Figure 1. Hope Duncan, *What if the jellyfish became encrusted with calcium carbonate?*, 2018 (detail).

Figure 2. Hope Duncan, *What if the jellyfish became encrusted with calcium carbonate?*, 2018 (detail).

These interactions can be likened to society's interactions with and responses to issues such as ocean acidification. There are those who do not really want to know about it; those who dabble, but fail to fully commit; and those who jump right in. Over time, the latter group will bring back friends who initially passed by or just dabbled and, with a degree of coercion, will get their cautious friend to fully commit, resulting in the latter having a great experience and the two walking away smiling and talking about it. Our hope is that, as with our jellyfish exhibit, people will introduce friends to global issues that matter, and that in the end this will trigger a domino effect whereby people get excited about the experience and challenge of change for the better.

Hope Duncan is a contemporary fibre artist who uses natural fibres, mainly wools, in combination with traditional and experimental weaving, spinning and tufting techniques to create works that respond to social, environmental and national issues. Duncan creates pieces that require the viewer to look closer and spend time reading her work. In so doing, Duncan invites people to think about the issues raised by her work and begin conversations outside the works.

1. Hawai'i Pacific University, Oceanic Institute, *Aqua Facts* [n.d.], https://oceanicinstitute.org/aboutoceans/aquafacts.html.
2. Mattison, 2015. [not in reference list]
3. Average global surface ocean pH has already fallen from a pre-industrial value of 8.2 to 8.1, corresponding to an increase in acidity of about 30%. Values of 7.8–7.9 are expected by 2100, representing a doubling of acidity. Values of 7.8–7.9 are expected by 2100, representing a doubling of acidity. "What is Ocean Acidification" https://www.otago.ac.nz/oceanacidification/whatisoa/index.html
4. *Ocean Acidification Process*, 9 December 2010, http://www.climatecentral.org/gallery/graphics/ocean-acidification-process
5. Alison F Takemura, "Ocean Acidification Affects Fish Spawning: Researchers Report the First Evidence that Acidified Waters Alter the Ocellated Wrasse's Reproductive Behaviour in the Wild," *The Scientist*, 26 July 2016, https://the-scientist.com/the-nutshell/ocean-acidification-affects-fish-spawning-33137.
6. Jason Hall-Spencer, "Attack of the Jellies: The Winners of Ocean Acidification," *The Conversation*, 3 December 2015, https://theconversation.com/attack-of-the-jellies-the-winners-of-ocean-acidification-50576.
7. J Hall-Spencer and R Allen, "The Impact of CO_2 Emissions on 'Nuisance' Marine Species," *Research and Reports in Biodiversity Studies*, 2015:4 (2015), 33-46, doi.org/10.2147/RRBS.S70357.